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ANALYSIS OF URANIFEROUS BITUMENS FROM THE MAGDALEN ISLANDS

by

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INTRODUCTION

Twelve samples of sand and rock from the Magdalen Islands were submitted to the Research on Bituminous Substances Section of the Energy Research Laboratories by Dr. Hugh Dunsmore of the Geological Survey of Canada (G.S.O.C.) for analysis. This laboratory was asked to determine the presence of hydrocarbons in the samples and to suggest a coal or petroleum precursor as the source of this organic material.

EXPERIMENTAL

Description of Sample:

The samples were composed of sand with dark particulates or rocks containing specs or narrow bands of "coal-like" material.

Sample Treatment:

Where feasible, tweezers were used to remove the darker particles from the sand samples. Chips of dark material were broken from the rock samples. All samples were ground with mortar and pistle to under 40 mesh in particle size.

Samples of coal, asphaltenes from Athabasca bitumen, commercial peat and peat moss were also analyzed by pyrolysis gas chromatography for comparison. The analysis conditions are given in Table I. Table 2 gives a list of the various types of coals used and their major hydrocarbon pyrolysis products.

RESULTS AND DISCUSSION

Chromatograms of the pyrolysis products of the coals, asphaltenes and peats are shown in Figures 1, 2 and 3. The high volatile coals, peats and asphaltenes generate relatively larger quantities of propylene than do the low volatile coals. Pyrograms of the G.S.O.C. samples are shown in Figures 4 and 5. The numbers (DAB-1, etc.) on the pyrograms refer to the G.S.O.C. reference file.

The pyrograms indicate the presence of organic material in the samples submitted by the Geological Survey of Canada. Although the generation of large amounts of propylene, as in asphaltenes and peat, may be an indication as to the source of the carbonaceous material, results under these analytical conditions are inconclusive.

TABLE I

Chromatographic Conditions For Analysis of Uraniferous Bitumens

Gas Chromatograph: Vicoreen model 4000 with pyrolysis unit.
Column: 6' x 1/8" o.d. stainless steel packed with Porapak Q, 80-100 mesh
Carrier Gas: Helium at 40 cc/minute
Oven Temperature: $60^{o}C$
Detector: Flame Ionization at $300^{o}C$
Recorder input: 1 millivolt full scale HP 5100 B
Integrator: Spectra-Physics System I
Sampling: weigh sample into stainless steel boat or Cahn electrobalance and insert into injection port of pyrolyzer.
Pyrolysis: ambient to $850^{o}C$ in 12 seconds

TABLE 2

Percentages of Gases Evolved During Pyrolysis of Coals				
Sample	Gases (%) *			% Sample Loss**
	Methane	Ethylene	Ethane	
High Volatile Coal (devco mix)	56.52	38.22	5.26	43.48
Med. Vol. Coal	66.66	30.94	2.40	20.63
Semianthracite	82.72	16.33	0.95	12.58
Lignite	52.61	42.89	4.50	39.93

* These percentages refer to the total of the 3 major organic gases evolved (methane, ethylene and ethane)

** Loss include water-samples have not been dried

The silica columns (Nos. 1, 2) were packed using ordinary chromatographic pump (6000 psi) and thus higher column efficiencies, usually attained by the use of slurry packers, were not possible. Selectivity on the Lichosorb-NH_2 column was low, and the retentions were too short to be of practical use in conjunction with the mass spectrometer.

The C_{18} column deteriorated after 4 months of continuous use with the standard polynuclear aromatic compounds and those derived from the hydrocracked bitumen. This was caused by irreversible sorption of the higher ring type compounds, especially those from the bitumen fractions. The use of a precolumn is suggested to alleviate this problem. The application of a solvent gradient system should also improve the separation as obtained under isocratic conditions.

Although the LC separation system silica-C_{18}/water-acetonitrile is so far, offering optimal possibilities for PAH characterization in bitumen samples (as confirmed by our experiments and published literature), yet it limits the characterization to those PAH that are soluble in acetonitrile. A variety of bonded chromatographic phase sorbents and mobile phases should be checked for their PAH selectivity.

The present LC sorbent-mobile phase systems resolve PAH on the basis of chemical affinity. Characterization of PAH's on geometrical basis, e.g. ring-type distribution, average diameter of ring systems or average molecular size could be more informative. Mobile phases that offer strong structure-temperature dependence (e.g. H_2O-soap mesophase) might be effective in separations based on the geometry of the ring systems.

The following experimental attempts are being performed:

- The temperature behaviour of water-potassium Laureate phase.
- Temperature dependence of PAH fluorescence spectra in H_2O-soap phases.
- Slurry packing of various columns.

Sample Size

Various combinations of sample concentrations and loop volume were tried. The appropriate sample concentration is sought for the following reasons:

(1) Reproducible retention data cannot be realized unless the retentions fall on the linear portion of the sorption isotherm.

(2) Concentration of the hydrocarbon material under the resolved liquid chromatographic peak should be sufficient to meet the mass spectrometric detection limits.

(3) The concentration should be within the linear response limits of the UV detector.

A loop size of 250 µl, and sample concentration of 60 mg/4 ml acetonitrile were satisfactory for fraction collection. The process was repeated 3-5 times to collect a sample that meets the above requirements.

Temperature Gradient

The elution sequences of some polynuclear aromatic hydrocarbons from the Chromegabond-C_{18} column with aqueous acetonitrile have been found to be influenced by temperature changes (2). The use of an efficient temperature gradient system would be useful to achieve complete elution of material by restraining resolution. A temperature range of 15 to 60°C was found suitable for this separation.

Collecting Cuts for GC and MS Analysis

The water has to be removed from the aqueous fractions collected from the HPLC columns before they are introduced to GC separations and mass spectrometric identification. The attempt to remove water by evaporation and nitrogen flushing caused excessive sample losses. It was possible to remove water by adding benzene to the aqueous acetonitrile cut. Two layers were formed, and the PAH were salted out by adding NaCl to the mixture. The organic phase was then separated and evaporated to 0.5 ml for further MS analysis.

Gas Chromatographic Analysis

The following eight pure PAH were used for calibrating the gas chromatographic column: phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, m-terphenyl, chrysene and perylene.

The resolution of the PAH bitumen fractions obtained from liquid chromatography was very poor on the OV-1 column due to the complexity of the samples. When a similar gas chromatographic system was interfaced with the mass spectrometer, considerable contamination from carboxylic acid esters was detected in the liquid chromatographic samples. Attempts are being made to eliminate this source of contamination.

From a literature search on the analysis of PAH it has been decided to use glass capillary chromatography as a means for separating the components under investigation. Two types of stationary phases will be employed in the study: OV-101 (6), and SE-52 (7,1). The studies of Grimmer (6), Giger (7) and Hites (1) will assist in establishing experimental conditions.

Mass Spectrometry

The work on the mass spectrometer resulted mainly in developing sample size to obtain peak concentrations that are identifiable within the sensitivity limits of the machine. Spectra were preliminarily characterized as to the number of aromatic rings in the separated PAH fractions.

Extensive library data search and MS scanning of pure compounds would be necessary for thorough identification of the PAH fractions. A computer search will be done for the major components (as expected from the HPLC and GC results) as well as the unknown compounds. The spectra will also be interpreted for homologue distribution patterns. Selective ion monitoring for certain polynuclear aromatics (carcinogenic suspects) is planned.

Spectrofluorometric Analysis

The spectrofluoremeter is the most specific LC detector. It has been used in this work in conjunction with the UV detector. It could be particularly useful for the identification of the PAH pure compounds that had undergone photomodification during storage.

Fluorescence spectra of the majority of PAH are not affected by alkyl substitution on the ring system (insignificant betachromic effect). Spectrofluorometry is the only method which could allow characterization of ring size distribution in the PAH samples (8). It is also the appropriate method for characterization and identification of the non-volatile materials in the bitumen which cannot be identified by GC-MS.

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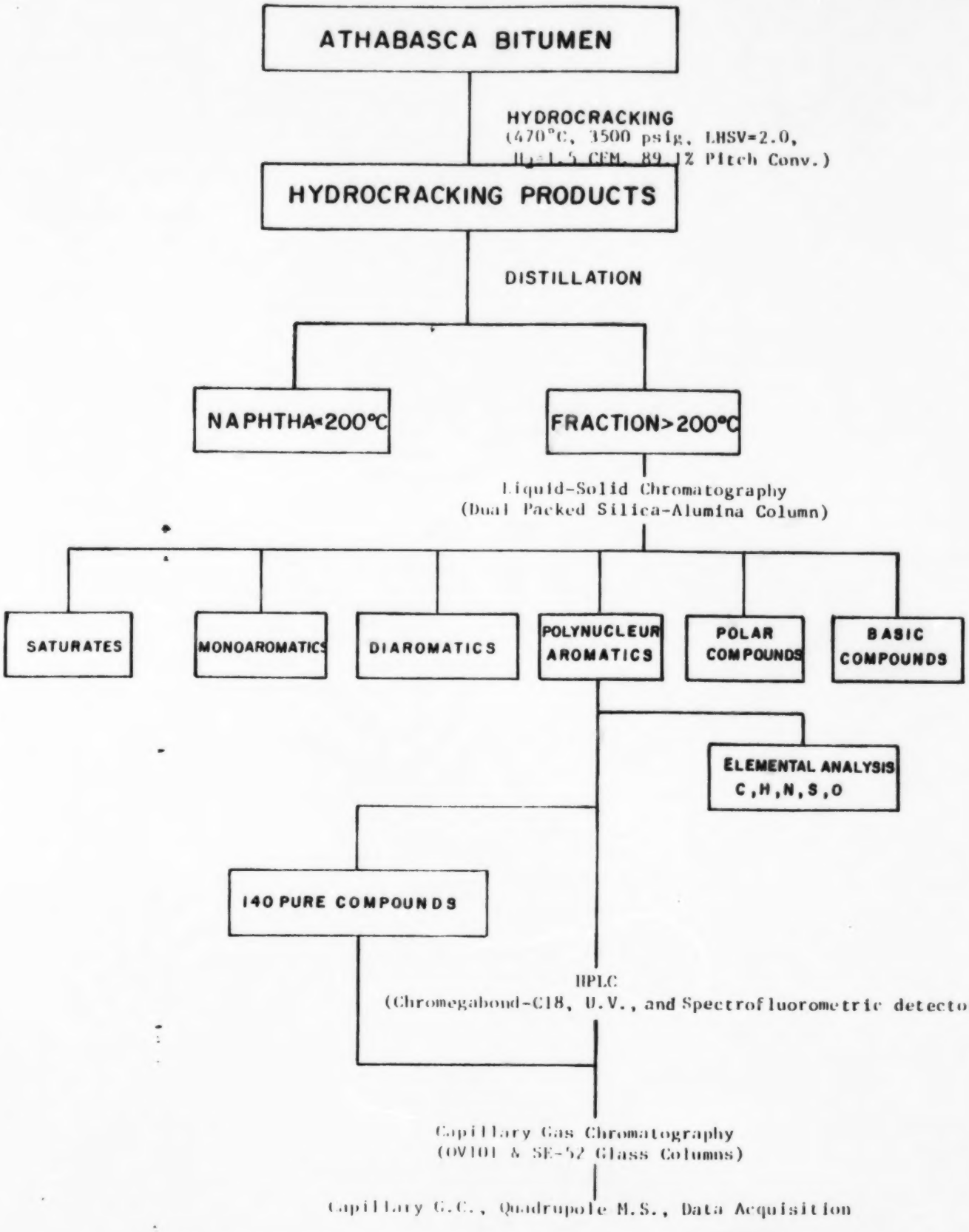

Separation and Identification Schematic of Polynuclear Aromatics in Athabasca Bitumen